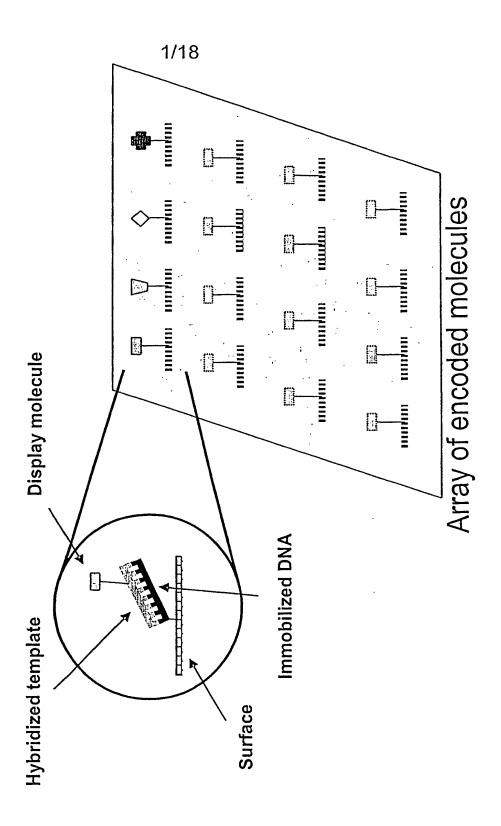
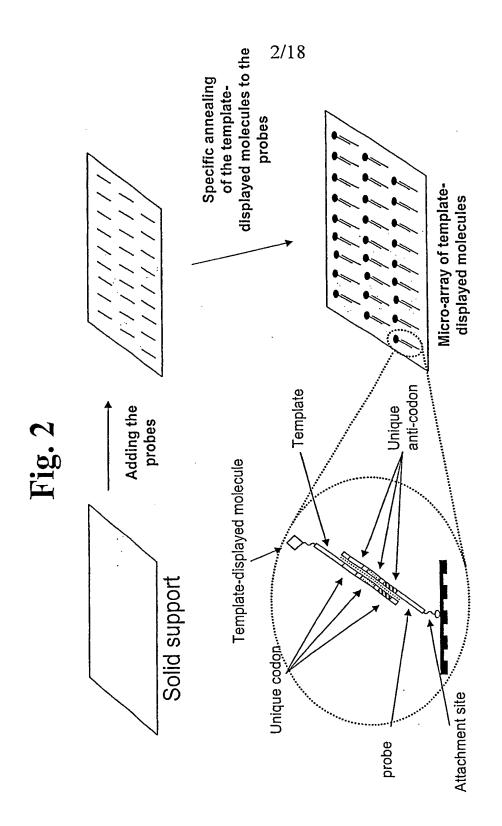
Fig.





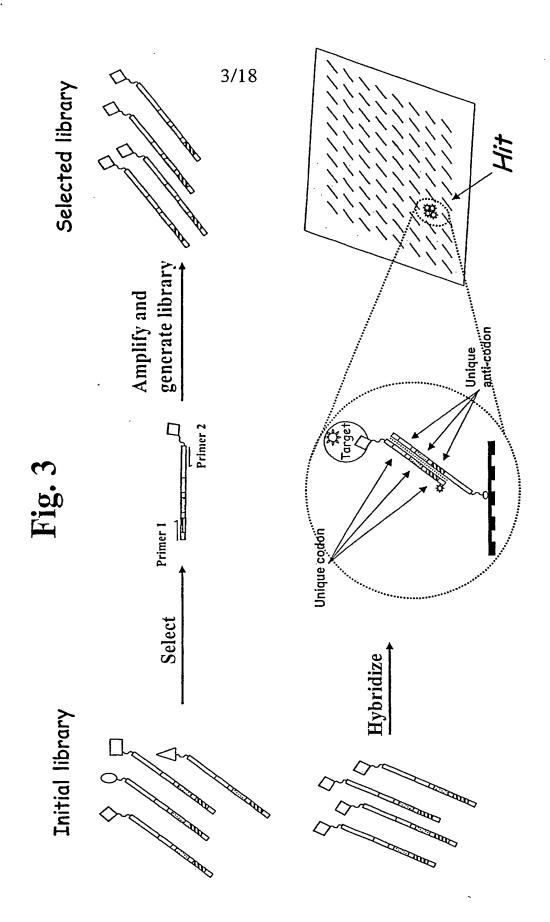
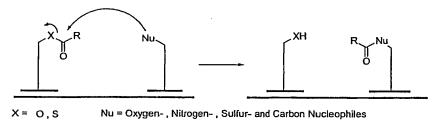


Fig. 4

A. Acylating monomer building blocks - principle



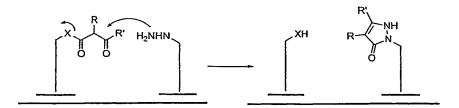
B. Acylation

Amide formation by reaction of amines with activated esters



C. Acylation

Pyrazolone formation by reaction of hydrazines with β -Ketoesters



D. Acylation

Isoxazolone formation by reaction of hydroxylamines with

β-Ketoesters

E. Acylation

Pyrimidine formation by reaction of thioureas with β -Ketoesters

F. Acylation

Pyrimidine formation by reaction of ureas with Malonates

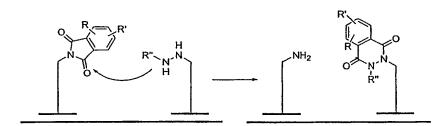
G. Acylation

Coumarine or quinolinon formation by a Heck reaction followed by a nucleophilic substitution

$$X = O,S$$
 $X' = Halogen, OTf, OMs$ $Z = O, NH$

H. Acylation

Phthalhydrazide formation by reaction of Hydrazines and Phthalimides

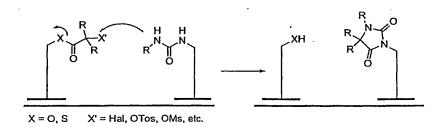


I. Acylation

Diketopiperazine formation by reaction of Amino Acid Esters

J. Acylation

Hydantoin formation by reaction of Urea and α -substituted Esters



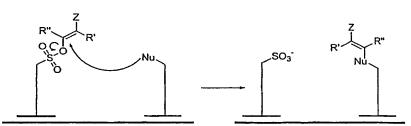
K. Alkylating monomer building blocks - principle

Alkylated compounds by reaction of Sulfonates with Nucleofiles



Nu = Oxygen- , Nitrogen- , Sulfur- and Carbon Nucleophiles

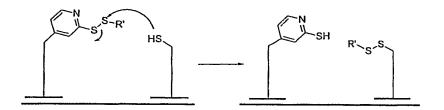
L. Vinylating monomer building blocks - principle



Z = CN, COOR, COR, NO₂, SO₂R, S(=O)R, SO₂NR₂, F Nu = Oxygen- , Nitrogen- , Sulfur- and Carbon Nucleophiles

M. Heteroatom electrophiles

Disulfide formation by reaction of Pyridyl disulfide with Mercaptanes



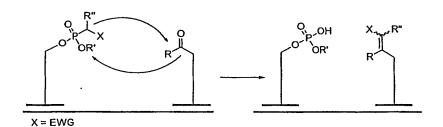
N. Acylation

Benzodiazepinone formation by reaction of Amino Acid Esters and Amino Ketones

$$X = 0, S$$

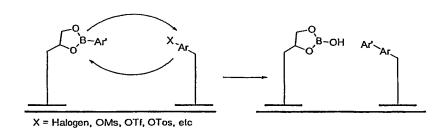
O. Wittig/Horner-Wittig-Emmons reagents

Substituted alkene formation by reaction of Phosphonates with Aldehydes or Ketones



P. Arylation

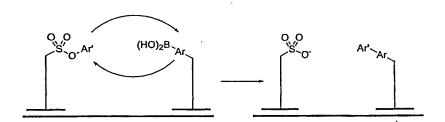
Biaryl formation by the reaction of Boronates with Aryls or Heteroaryls



Q. Arylation

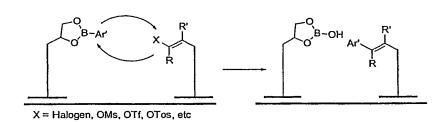
Biaryl formation by the reaction of Boronates with Aryls or Heteroaryls

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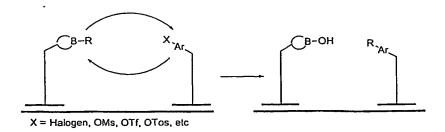
R. Arylation

Vinylarene formation by the reaction of alkenes with Aryls or Heteroaryls



S. Alkylation

Alkylation of arenes/hetarens by the reaction with Alkyl boronates

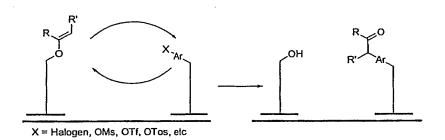


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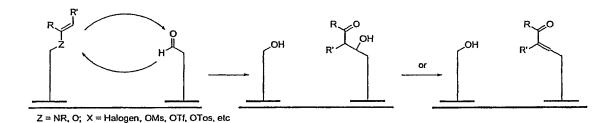
T. Alkylation

Alkylation of arenas/hetarenes by reaction with enolethers



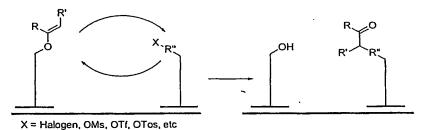
U. Condensations

Alkylation of aldehydes with enolethers or enamines

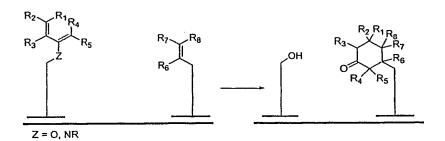


V. Alkylation

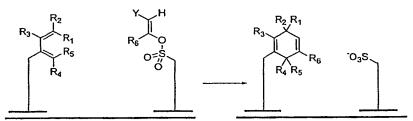
Alkylation of aliphatic halides or tosylates with enolethers or enamines



W. [2+4] Cycloadditions



X. [2+4] Cycloadditions



Y, CN, COOR, COR, NO2, SO2R, S(=O)R, SO2NR2, F

Y. [3+2] Cycloadditions

Y, CN, COOR, COR, NO $_2$, SO $_2$ R, S(=0)R, SO $_2$ NR $_2$, F

Z. [3+2] Cycloadditions

Y, CN, COOR, COR, NO2, SO2R, S(=0)R, SO2NR2, F

Fig. 5

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Nucleophilic substitution reaction

R-X		R'-0"	•	ETHERS	$R \stackrel{S}{\longrightarrow} R \stackrel{+}{\longrightarrow} R \stackrel{-}{\longrightarrow} R \stackrel{S}{\longrightarrow} R $	THIOAMIDES
R-X	+	R'-S	 R-S-R'	THIOETHERS	O-K, HN	J—K.
R-X	+	R'-NH ₂	 R-N-R' H	sec- AMINES	R-(+ R*-NH ₂) AMIDES I-R"
			R [™] —Ņ-R' Ř	tert-AMINES	S	THIOAMIDES
*	+	R'0"	 HO OR'	β-HYDROXY ETHERS	$R \stackrel{S}{\longleftarrow} + R"-NH_2 \longrightarrow R \stackrel{S}{\longleftarrow} HN$	
			HO SR'		R"-X + N OH N N	
%	+	R'-NH ₂	 HO NHR'	β-HYDROXY AMINES	R"-SO ₂ Cl + H R-N-R'	P' 2-N SULFONAMIDES R
RN	+	R'-0"	 RHN OR'	β-AMINO ETHERS	R'-X + R-∳	Z' DI- AND TRI- -R' FUNCTIONAL Z COMPOUNDS
₹—(0 0-R'	+	R"NH ₂	 R-{ HN-R"	AMIDES	$R' \longrightarrow \begin{pmatrix} 0 & + & R \longrightarrow \begin{pmatrix} Z' & & & \\ & 2 & & & \end{pmatrix}$	Z' O DI- AND TRI- FUNCTIONAL COMPOUNDS
₹{ SR'	+	R"—NH ₂	 R{ HN-R*	AMIDES	$Z',Z = COOR, CHO, COR,$ $NO_2, SOR, SO_2R,$	

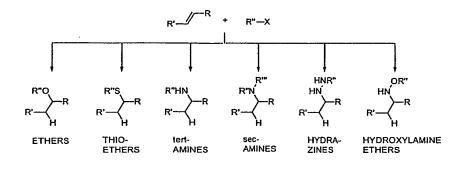
Aromatic nucleophilic substitution

Transition metal catalysed reactions

SUBSTITUTED AROMATIC COMPOUNDS

$$\begin{split} \text{Nu} &= \text{Oxygen-} \text{, Nitrogen-} \text{, Sulfur- and Carbon Nucleophiles} \\ \text{X} &= \text{F, Cl, Br, I, OSO}_2\text{CH}_3, \text{OSO}_2\text{CF}_3, \text{OSO}_2\text{TOL, , , etc.} \\ \text{Z', Z} &= \text{COOR} \text{, CHO} \text{, COR} \text{, CONR''}_2, \text{COO'}, \text{CN} \text{,} \\ \text{NO}_2 \text{, SOR} \text{, SO}_2\text{R} \text{, SO}_2\text{NR''}_2 \text{, ect.} \end{split}$$

Addition to carbon-carbon multiplebonds



Z = H, Alkyl, Z', Ar

Z" = COOR, CHO, COR, CONR"2, CN, NO2, SOR, SO2R, SO2NR"2,, ect.

R = R', = R'', = Z

$$Z$$
 Z'
 $+$
 Z''
 Z''
 Z''
DI- AND TRI-
FUNCTIONAL
ALKENES

Z = H, Alkyl, Ar,

Z" = Z', Alkyl, Ar,

Z' = COOR, CHO, COR, CONR"2, CN, NO2, SOR, SO₂R, SO₂NR"₂, ect.

Cycloaddition to multiple bounds

Z = COOR, CHO, COR, COOH COAr CN, NO2, Ar, CH2OH, CH2NH2, CH2CN, SOR, SO2R etc.

R = H, Alkyl, Ar, Z X = 0, NR, CR2, S,

Addition to carbon-hetero multiple bonds

Z = COOR, CHO, COR, SOR, SO2R, CN, NO2, act. R = R', H, Alkyi, Ar,

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Fig. 6

A. Linker for the formation of Ketones, Aldehydes, Amides and Acids

B. Linker for the formation of Ketones, Amides and Acids

C. Linker for the formation of Aldehydes and Ketones

D. Linker for the formation of Alcohols and Acids

E. Linker for the formation of Amines and Alcohols

F. Linker for the formation of Esters, Thioesters , Amides, and Alcohols

$$R' \circ \stackrel{R-XH}{\longrightarrow} R' \circ OH + \stackrel{O}{R^*} X$$
 $X = O, S, NHR, NR_2$

G. Linker for the formation of Sulfonamides and Alcohols

H. Linker for the formation of Ketones, Amines and Alcohols

I. Linker for the formation of Ketones, Amines, Alcohols and Mercaptanes

J. Linker for the formation of Biaryl and Bihetaryl

$$\begin{array}{c} O \\ B - Ar' \end{array} \xrightarrow[PdCl_2/Blnap]{} Ar - x \\ 2M K_3 PO_4 \end{array} P \begin{array}{c} O \\ R \end{array} B - OH \ + \ Ar' - Ar \end{array}$$

K. Linker for the formation of Benzyles, Amines, Anilins Alcohols and Phenoles

L. Linker for the formation of Mercaptanes

TCEP = tris(2-carboxyethyl)phosphine

M. Linker for the formation of Glycosides

N. Linker for the formation of Aldehydes and Glyoxylamides

O. Linker for the formation of Aldehydes, Ketones and Aminoalcohols